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catena-Poly[[bis(α -thenoyltrifluoroacetato)-copper(II)]- μ -1,4-di-4-pyridyl-2,3-diazabuta-1,3-diene]

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Key indicators

Single-crystal X-ray study
 $T = 294\text{ K}$
 Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
 Disorder in main residue
 R factor = 0.036
 wR factor = 0.095
 Data-to-parameter ratio = 11.8

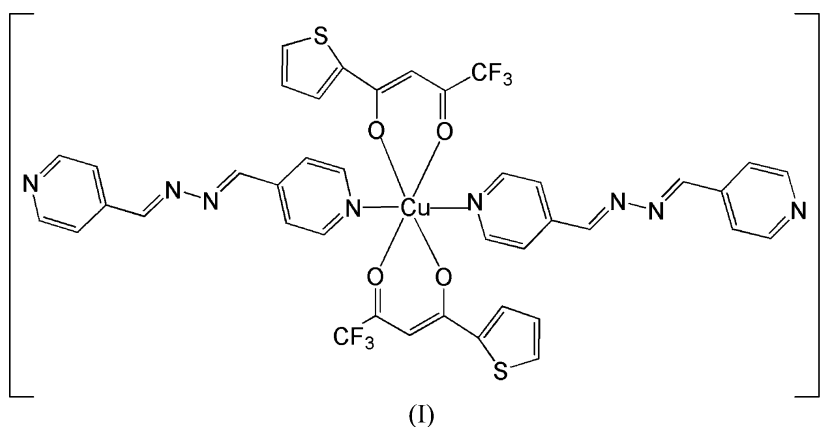
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

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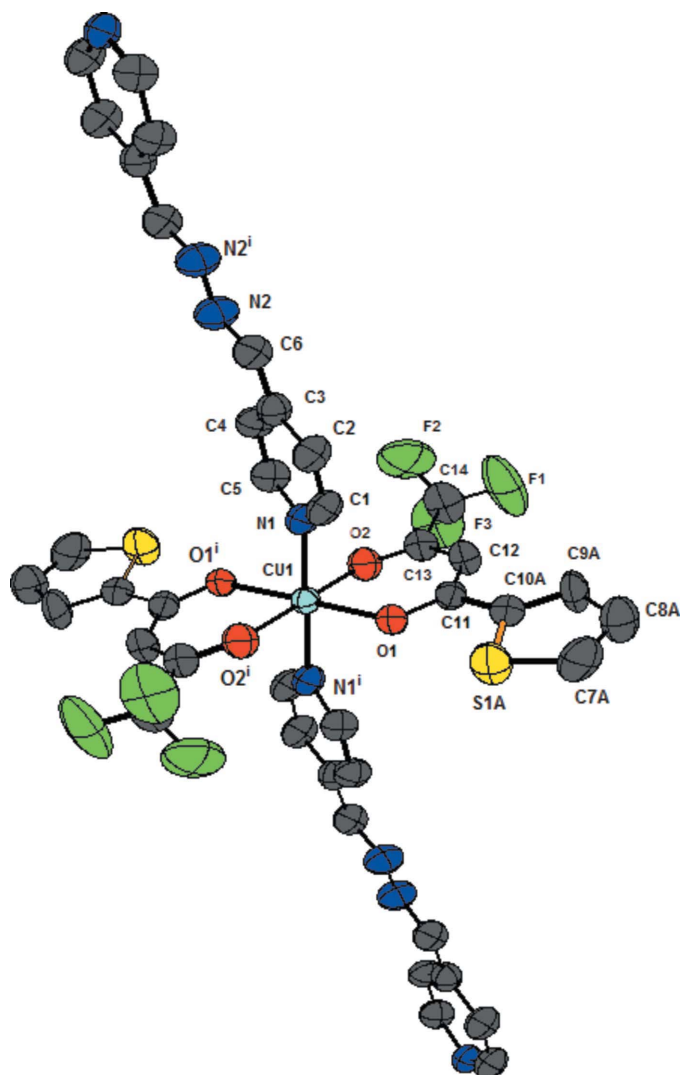
In the one-dimensional title polymer, $[\text{Cu}(\text{C}_8\text{H}_4\text{F}_3\text{O}_2\text{S})_2(\text{C}_{12}\text{H}_{10}\text{N}_4)]_n$ or $[\text{Cu}(L)_2(\text{tta})_2]$ [tta is α -thenoyltrifluoroacetato and L is 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene], Cu^{2+} lies on a center of inversion. It is axially coordinated by two pyridyl N atoms from two different L ligands and equatorially coordinated by four O atoms from two chelating tta ligands. The ligand L propagates the one-dimensional chain structure by serving as a bridging ligand between two Cu octahedra *via* Cu–N coordinate bonds.

Comment

The synthesis of new coordination polymers has interested chemists and materials scientists because of the potential applications of these materials in a variety of areas, including catalysis, optical applications and gas sorption (Atto *et al.*, 1999; Wang *et al.*, 1995; Chen *et al.*, 1998). Our group has been interested in the synthesis of new N,N' -type organic ligands for the construction of new inorganic–organic coordination polymers. To this end, we have been successful in the synthesis of several Schiff base ligands, such as 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene, which have resulted in the generation of many new coordination compounds (Dong *et al.*, 2000; Dong *et al.*, 2000a). The title compound, *catena*-poly $[\text{Cu}(L)_2(\text{tta})_2]$ (tta is α -thenoyltrifluoroacetato), (I), is a new example of a one-dimensional coordination polymer that uses an N,N' -type Schiff base ligand in its construction.

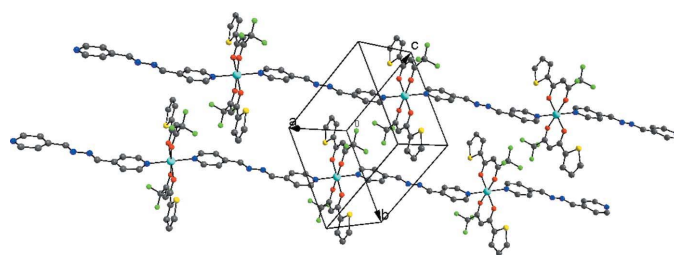


Compound (I) was prepared by the room-temperature layering reaction of $\text{Cu}(\text{tta})_2$ in dichloromethane with the ligand L in ethanol. Emerald-green crystals formed upon diffusion of the two solutions into one another over the course of several weeks, and a suitable single crystal was selected for the structure determination. In (I), Cu^{2+} centers are found in a

**Figure 1**

The molecular structure of (I), with the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. Cu atoms are shown in turquoise; O, red; N, blue; F, green; S, yellow; C, black. H atoms have been omitted. Only the major disorder component is shown. [Symmetry code: (i) $1 - x, 1 - y, -z$.]

distorted octahedral coordination environment and they are located on sites of crystallographic inversion symmetry. Consequently, each Cu^{2+} center is coordinated by pairs of symmetry-related ligands. A symmetry-related pair of tta ligands occupies the equatorial positions, with each tta ligand coordinated through its O atoms in a bidentate fashion. Two pyridyl N donor atoms, one from each of two different symmetry-related *L* ligands, complete the octahedral coordination by occupying the axial positions. The average Cu—O bond length is 2.085 Å, the Cu—N bond distance is 2.1062 (19) Å, and the intrachain distance between successive Cu centers is approximately 15.4 Å. The Cu—O and Cu—N distances are typical (Yang *et al.*, 2001; Lingafelter & Braun, 1966), and the $\text{Cu} \cdots \text{Cu}$ distance provides an estimate of the length of *L*. The octahedrally coordinated Cu^{2+} centers are linked into one-dimensional chains by *L*, with each N-atom donor of a single *L* coordinated to two different Cu centers.

**Figure 2**

View of the crystal packing in (I). H atoms have been omitted.

The packing arrangement of the one-dimensional chains is shown in Fig. 2, where it can be seen that the chains extend approximately along the body diagonal of the unit cell, in the crystallographic $[1\bar{1}\bar{1}]$ direction.

Experimental

Synthesis of the ligand *L* was accomplished by minor variation of the published literature procedure, using 4-pyridine carboxaldehyde rather than 3-pyridine carboxaldehyde (Dong *et al.*, 2000*b*). $\text{Cu}(\text{tta})_2$ was prepared in bulk as follows: thenoyltrifluoroacetone (Htta, 10 mmol) and NaOH (10 mmol) were added to ethanol (50 ml) to deprotonate the tta ligand (tta^-). $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (5 mmol) was then added to the tta[−] solution to produce $\text{Cu}(\text{tta})_2$ as a light-green precipitate. The precipitate was harvested by vacuum filtration and washed with cold ethanol for use in the next step. The title compound was obtained by slow diffusion of a solution containing *L* (0.1 mmol) dissolved in ethanol (8 ml) into a solution of $\text{Cu}(\text{tta})_2$ (0.1 mmol) dissolved in dichloromethane (8 ml). Initially, the two solutions were carefully layered, and emerald-green crystals appeared at the interface of the two solutions after several weeks.

Crystal data

$[\text{Cu}(\text{C}_8\text{H}_4\text{F}_3\text{O}_2\text{S})_2(\text{C}_{12}\text{H}_{10}\text{N}_4)]$

$M_r = 716.12$

Triclinic, *P*1

$a = 8.6890$ (11) Å

$b = 9.7518$ (13) Å

$c = 10.2035$ (13) Å

$\alpha = 116.398$ (2)°

$\beta = 99.417$ (2)°

$\gamma = 97.919$ (2)°

$V = 741.99$ (17) Å³

$Z = 1$

$D_x = 1.603$ Mg m^{−3}

Mo $K\alpha$ radiation

Cell parameters from 4033 reflections

$\theta = 2.3\text{--}25.1^\circ$

$\mu = 0.96$ mm^{−1}

$T = 294$ (2) K

Prism, green

$0.30 \times 0.24 \times 0.20$ mm

Data collection

Bruker SMART APEX CCD diffractometer

ω scans

Absorption correction: multi-scan (SADABS; Bruker, 2001)

$T_{\min} = 0.658$, $T_{\max} = 0.830$

4780 measured reflections

2577 independent reflections

2495 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$

$\theta_{\max} = 25.1^\circ$

$h = -10 \rightarrow 10$

$k = -11 \rightarrow 11$

$l = -12 \rightarrow 12$

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.095$

$S = 1.07$

2577 reflections

218 parameters

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0508P)^2 + 0.2977P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.31$ e Å^{−3}

$\Delta\rho_{\min} = -0.36$ e Å^{−3}

Table 1

Selected geometric parameters (Å, °).

Cu1—O1	1.9759 (15)	Cu1—O2	2.1950 (18)
Cu1—N1	2.1062 (19)	N2—N2 ⁱ	1.404 (4)
O1 ⁱⁱ —Cu1—O1	180	O1—Cu1—O2	88.01 (6)
O1—Cu1—N1	90.97 (7)	N1—Cu1—O2	87.16 (7)
N1 ⁱⁱ —Cu1—N1	180	O2 ⁱⁱ —Cu1—O2	180

Symmetry codes: (i) $-x, -y + 2, -z + 1$; (ii) $-x + 1, -y + 1, -z$.

H atoms were placed in geometrically idealized positions and included as riding atoms with C—H distances fixed at 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The thiophene ring of the tta ligand is disordered, and the disorder was modeled as a two-component rotational disorder about the *ipso* carbon bond (C10—C11). The two disorder components lie essentially in the same plane. The geometry of the minor component (C7B—C10B/S1B) was restrained to be similar to that of the major component (C7A—C10A/S1A). The pivot atom C10A,B is common to both components, and atoms less than 0.5 Å from their disorder counterparts were assigned equal displacement parameters. The total occupancy was restrained to sum to unity. The final refined occupancies are $A/B = 0.773(3)/0.227(3)$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

SHELXTL (Sheldrick, 2000); software used to prepare material for publication: *SHELXTL*.

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